Reduction of Ozone Fading of Copper Phthalocyanine Dyes by Non-traditional Antiozonants

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Abstract

Ozone fading of printed images has been an important issue in digital imaging industries. Copper phthalocyanine dyes, widely used in imaging products, are highly susceptible to ozone fading. Mixing of dyes with conventional antiozonants, used in other non-imaging industrial products, is usually not suitable for systems where the dyes are required to be in solution, due to the relatively lower solubility of these antiozonants in aqueous or solvent systems. Some of these efficient antiozonants also react with air, resulting in highly colored compounds, which make them unsuitable for imaging products. The presence of suitable functional groups in the antiozonant molecules can reduce both these problems. The results presented in this paper show that several compounds, which are not used as typical antiozonants, improve ozone stability of copper phthalocyanine dyes to significant extents, with minimal colorimetric shifts. The effects of substituents on these antiozonant molecules and the possible mechanisms of the antiozonant effect are also discussed in this paper.

Introduction

Copper phthalocyanine (CuPC) dyes are extensively used in imaging systems because of their high spectral absorptivity, solubility in various common organic solvents and light fastness. However, these dyes are also susceptible to ozone fading under various ambient conditions. Although phenylenediamines are effective antiozonants for several commercial products, such as rubber, where the oxidation due to exposure to ambient ozone can cause destruction of certain essential properties, they are not suitable as antiozonants for imaging products because these compounds undergo severe discoloration when exposed to air or ozone. Aminoanthraquinone (AAQ) dyes contain the same functional groups that are responsible for antiozonant property of p-phenylenediamines, but also contain electron withdrawing carbonyl groups in the fused ring systems, which minimize the formation of colored oxidation products, without any significant reduction of their effectiveness as antiozonants. When these dyes are mixed with a CuPC dye, the ozone stability of the mixed dye system is better than the CuPC dye. Due to the relatively lower spectral absorptivity of the AAQ dyes compared to CuPC dyes the absorption spectra of the mixtures are not significantly different from the CuPC dyes. The AAQ dyes also contain other groups of varying electronegativities. Several AAQ dyes, with substituents of varying electronic properties have been tested with a CuPC dye to determine the correlation between structure and antiozonant property.

Experimental Procedures

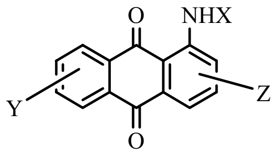
Test Methods

Solutions of mixtures of CuPC dye and AAQ dyes in organic solvents (n-butanol, methyl ethyl ketone, or other suitable solvent) were coated on PET sheets. The molar ratios of AAQ dyes to CuPC dye were maintained between 1 and 2. The coatings to be tested for ozone fading were exposed to ozone (~10 PPM), for definite periods of time. Ozone was produced in situ, by the direct photolysis of oxygen in the ambient air within a chamber equipped with a mercury-argon lamp. The extents of ozone stabilization due to the AAQ dyes were quantified by comparison of the reflection densities and values of colorimetric parameters, L*, a* and b* of the coated sheets before and after ozone exposure. Coatings of the AAQ dyes were also tested for ozone stability.

The oxidation potentials of the AAQ dyes were measured by cyclic voltammetry in acetonitrile using a Bioanalytical Systems (BAS) 100B/W potentiostat and BAS software. All experiments were run at ambient temperature under an atmosphere of high purity argon.

Aminoanthraquinones Tested

The selection of the AAQ dyes for testing with the CuPC dye was based on their spectral characteristics, with the intention to maintain the colorimetric change to a negligible extent. The aminoanthraquinone dyes used are represented by the general structure in Figure 1.



X = H, alkyl or aryl
Y, Z = -NH_2, -OH, -NH-, or halogen

Figure 1. General structure of the aminoanthraquinones dyes

Based on the substituents on the amino groups, the AAQ dyes tested are divided into three categories:

Type A: unsubstituted primary amino groups, –NH_2

Type B: alkyl or hydroxyalkyl substituted secondary amino groups, –NHR (R = alkyl or hydroxyalkyl)

Type C: aryl substituted secondary amino groups, –NHAr (Ar = alkyl substituted phenyl)

Other substituents on the rings are also present in many of these of dyes. The classification of the dyes is shown in Table I.

Table I. Classification of the AAQs Dyes Tested for Increasing Ozone Stability of CuPC

AAQ dyes	Amino groups and other substituents	
A-1	Diamine, –NH_2	Decreasing electron density on –NH_2 ↓
A-2	Monoamine, –NH_2	
A-3	Monoamine, –NH_2 ,with ring substituents, –OH and –Br	
A-4	Diamine, –NH_2, with fused ring containing >C=O groups	
B-1	Alkyl or hydroxyalkyl substituted secondary amines –NHR	Decreasing electron density on –NH– ↓
B-2		
B-3		
B-4		
B-5		
C-1	Aryl substituted secondary amines –NHAr	Decreasing electron density on –NH– ↓
C-2		
C-3		

Results and Discussion

Figures 2a and 2b show the effects of ozone exposure on spectra of coatings of a cyan CuPC dye and mixtures of CuPC with two AAQ dyes, A-1 and B-3, respectively, which have different electron densities on the amino groups. Significant reduction in density and spectral shift are observed for the CuPC dye, but the changes are much less for the dye mixtures. The dye system containing A-1, which has high electron density shows almost no change, whereas the system containing B-3, which has lower electron density on the amino group than A-1 appears to be less effective as antiozonant. No spectral changes were observed when the AAQ dyes were exposed to ozone under identical conditions. The data listed in Table II show the ozone stabilizing effects of the AAQ dyes tested with CuPC, as evident from the extent of retention of cyan density and delta E* (calculated from changes of values of L*, a* and b* after exposure to ozone), which is an indication of spectral shift.

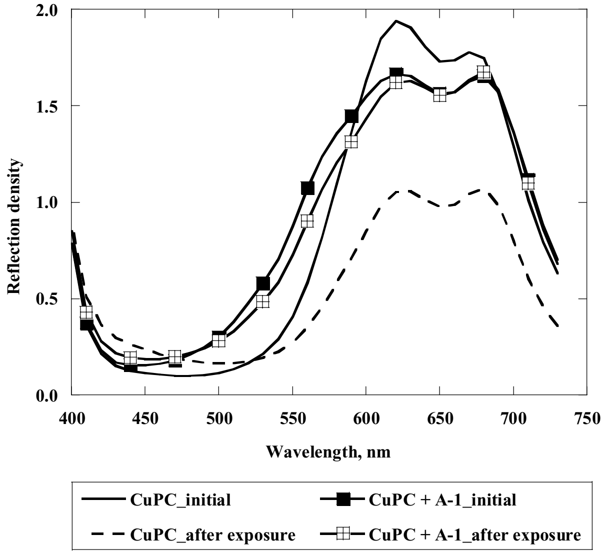


Figure 2a. Reflection spectra of coatings of CuPC with AAQ-A-1 before and after exposure to ozone

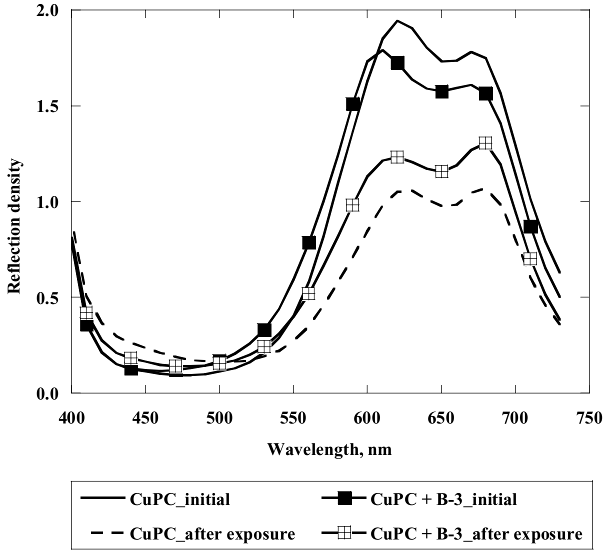


Figure 2b. Reflection spectra of coatings of CuPC with AAQ-B-3 before and after exposure to ozone

Table II. Effects of AAQ Dyes on Ozone Exposure of Coatings of Equimolar Ratios of CuPC and AAQ Dyes

Ozone Level = 10 ppm Exposure Time = 1 hour

Type of AAQ added	Cyan density retained	delta E*
None (CuPC only)	55%	24.7
A-1	98%	13.2
A-2	94%	8.5
A-3	82%	14.2
A-4	55%	18.1
B-1	86%	11.8
B-2	84%	12.2
B-3	78%	16.6
B-4	64%	15.1
B-5	62%	20.8
C-1	70%	14.8
C-2	61%	15.8
C-3	57%	19.0

The result shows that after exposure to ozone the cyan density of CuPC without any added AAQ is 55% of the initial density. In addition to decrease in cyan density, significant colorimetric shift, as indicated by delta E*, also occurs. The data in Table II indicate that the efficiency of the added dyes as antiozonants, as evident from the higher fraction of cyan density retained and lower colorimetric change (delta E*) depends on the electronic structure of the molecule. In each of the categories a decrease in the electron density on the amino group, due to the presence of substituents on nitrogen or other parts of the rings, results in a decrease of the antiozonant property of the dye.

The effects of increasing levels of the AAQ dyes on ozone stability of CuPC dye are shown in Table III. Greater ozone stability is observed at higher molar ratios of the more efficient dyes, e.g., A-3 and B-1. However, the increase is insignificant with less efficient dyes, i.e., C-3 and A-4.

Table III. Effects of Molar ratio Variation of AAQ to CuPC on Ozone Stability of CuPC

Ozone Level = 10 ppm, Exposure Time = 1 hour

AAQ	Molar ratio, AAQ : CuPC	Cyan density retained
A-3	1.0	82%
	1.5	91%
A-4	1.0	55%
	1.4	57%
B-1	1.0	86%
	2.0	93%
B-4	1.0	64%
	1.5	69%
B-5	1.0	62%
	1.8	72%
C-3	1.0	57%
	1.3	58%

In order to determine the effects of the AAQ dyes on the rates of density loss of CuPC dye due to exposure to ozone, mixtures of CuPC dye with each type of AAQ dyes were compared. Figure 3 shows the fraction of initial cyan density retained for each of the systems after definite intervals of time. Pseudo-first order rate plots for the loss of density are shown in Figure 4 and the calculated rate constants are listed in Table IV. It is apparent from these data that the substituents on the AAQ dyes have significant effect on the rate of density loss, which is a measure of the antiozonant property. The rate of density loss in presence of A-1 is more than an order of magnitude lower than of CuPC dye, or when mixed with a less efficient AAQ dye, such as B-3 or C-3. The data definitely indicate that electron donating groups on AAQ dyes, and consequently higher electron density on the amino groups of the dyes increases ozone stability of CuPC dye.

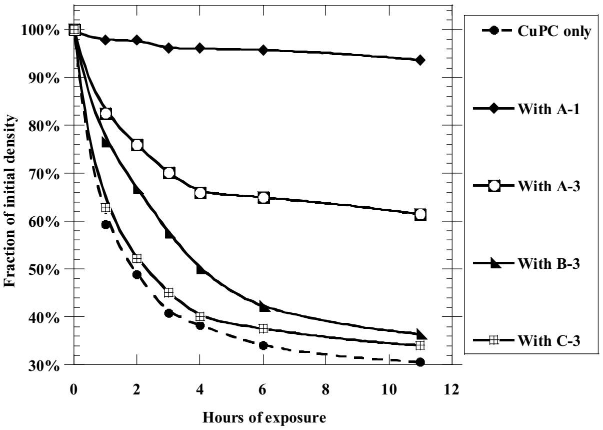


Figure 3. Effects of ozone exposure on reflection density of coatings of CuPC dye and mixtures of CuPC and AAQ dyes

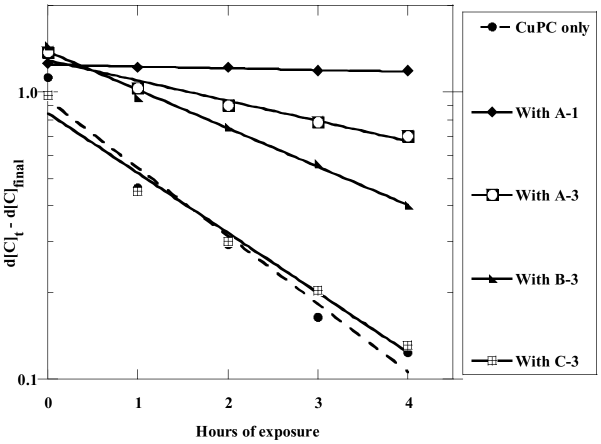


Figure 4. Pseudo-first order rate plots for density loss due to ozone exposure of CuPC dye and mixtures of CuPC and AAQ dyes

Table IV. Effects of AAQ Dyes on Ozone Stability of CuPC Dye : Pseudo-first order rate constants

AAQ Dye Added		Pseudo-first order rate constant for loss of cyan density, hr^{-1}
None (CuPC dye only)		0.545
A-1 (di $-NH_2$)	Decreasing electron density on –N< ↓	0.014
A-2 (mono $-NH_2$)		0.162
B-3 (–NHR)		0.308
C-3 (–NHAr)		0.480

Existing reports[1] indicate that the ozonation reactions of anilines and phenylenediamines proceed through electron transfer process and the rates of reactions correlate with the oxidation potentials. The electron density on the amino group of a molecule is expected to have a significant effect on the oxidation potential of the molecule. The mechanisms and products of oxidation of aromatic primary monoamines, diamines and secondary amines are different. [1,2] Thus it is reasonable to limit the comparison of the oxidation potentials of the AAQ dyes within the same molecular class, as defined in Table I and correlate the oxidation potentials with their effectiveness as antiozonants. Figures 5 shows a comparison of the cyclic voltammetric responses of dyes A-1 and A-4, both containing primary diamino groups but significantly different electron densities on the nitrogens on amino groups. The oxidation potential of A-1 is much lower than A-4, which correlates with their antiozonant properties. Figure 6 shows cyclic voltammograms of two dyes, B-3 and C-3 containing secondary amino groups with aliphatic and aromatic substituents, respectively. The dye B-3, containing a more electron rich amino group has lower oxidation potential than C-3, and is also a better antiozonant than C-3. The oxidation potentials of several other AAQ dyes of Types B and C, containing secondary amino groups are listed in Table V. It is obvious from the data that the oxidation potentials for Type B dyes containing aliphatic substituents on the amino groups are lower than Type C dyes containing aromatic substituents.

Table V. Oxidation Potentials* of AAQ Dyes Containing Secondary Amino Groups

AAQ Dye	1st Oxidation	2nd Oxidation	Reduction
B1	639 ± 1	1144 ± 1	-1093 ± 5
B2	642 ± 1	1138 ± 1	-1112 ± 1
B3	639 ± 1	1139 ± 1	-1112 ± 2
B4	715 ± 5	1005 ± 10	Not measured
B5	641 ± 2	1145 ± 2	-1089 ± 3
C1	782 ± 2	1191 ± 12	-1028 ± 2
C3	774 ± 2	1174 ± 15	

*All potentials are reported in mV vs SCE

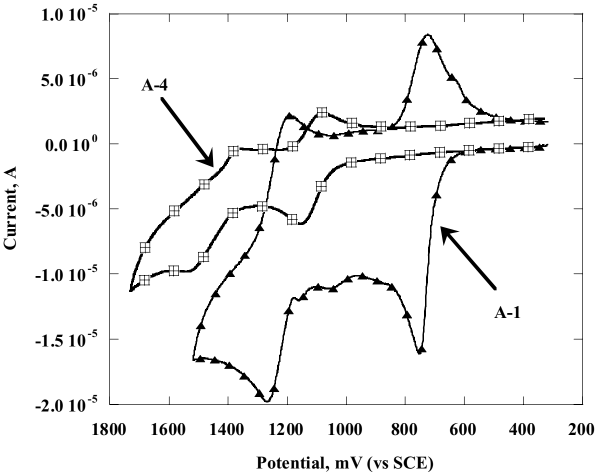


Figure 5. Cyclic voltammograms of AAQ dyes containing primary amino groups

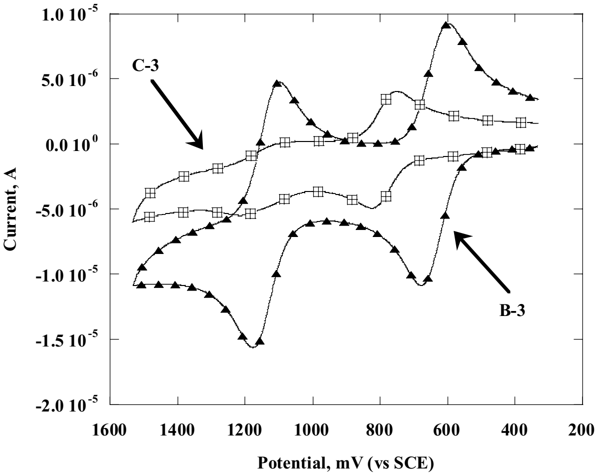


Figure 6. Cyclic voltammograms of AAQ dyes containing secondary amino groups

Conclusions

[1] Aminoanthraquinones dyes can be used as antiozonants for copper phthalocyanine dyes.

[2] Unlike p-phenylenediamine, which is a common antiozonant, aminoanthraquinones dyes do not exhibit any significant discoloration when exposed to ozone.

[3] Coatings of mixtures of copper phthalocyanine dyes with aminoanthraquinones dyes show less fading and spectral shift when exposed to ozone.

[4] The extent of ozone stability depends on the electronic structures of the antiozonants.

[5] The efficiency of the added aminoanthraquinone dye as antiozonant shows significant dependence on the substituents, which influence the electron density on the amino groups.

[6] Electron donating substituents increase and electron withdrawing substituents decrease the effectiveness of the dyes as antiozonants.

[7] Within each group of dyes, the oxidation potentials show a correlation with the electron densities on the amino groups and consequently the antiozonant property.

References

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Biography

Fariza Hasan, currently employed at Polaroid Corporation in Massachusetts, received her Ph.D. in chemistry from University of British Columbia, Vancouver, Canada. Her graduate and post-doctoral research included kinetics and mechanisms of various inorganic, organic and biochemical reactions. In her current position, she has been involved in optimization and design of several existing and new silver halide and digital imaging systems. She is a member of the IS&T and the American Chemical Society.